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# SPECIFICATION

## CERAMIC SUBSTRATE FOR A SEMICONDUCTOR PRODUCING/EXAMINING DEVICE

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### Technical Field

The present invention relates to a ceramic substrate for a semiconductor producing/examining device which is used mainly in semiconductor industries. Particularly, the invention relates to the ceramic substrate which has high fracture toughness value, and excellent adsorbing ability of a semiconductor wafer in case that the substrate is used for an electrostatic chuck, and has an excellent temperature rising and falling properties in case that the substrate is used as a hot plate (a heater).

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### Background Art

A semiconductor is an extremely important product which is required in various industries, and after an a semiconductor chip is produced in such a manner that a silicon single crystal is sliced into a predetermined thickness and a silicon wafer is produced, a plurality of semiconductor circuits and the like are formed on the silicon wafer.

At the step of producing this semiconductor chip, the silicon wafer placed on an electrostatic chuck is subjected to various processes such as CVD so that semiconductor circuits, elements and the like are formed. At this time, since corrosive gas is used as deposition gas, etching gas and the like, it is necessary to protect an electrostatic electrode layer from corrosion due to the gas. Moreover, since it is necessary to cause an adsorbing power, the electrostatic electrode layer is normally covered with a ceramic dielectric film and the like.

As this ceramic dielectric film, a nitride ceramic has been conventionally used. For instance, JP Kokai Hei 5-8140 discloses an electrostatic chuck which uses nitride such as aluminum nitride and the like. Moreover, JP Kokai Hei 9-48668



























nitride, but the firing is carried out for 3 hours at 1600°C and this temperature is too low to distribute the impurities locally in the grain boundaries sufficiently, and thus the thermal conductivity cannot be improved. Moreover, since the  
5 ceramic is fired at low temperature so that grains grow slowly, thus a grain diameter exceeds 10  $\mu\text{m}$ . Moreover, hardness and toughness value thereof is lowered therein, namely, this is designed based on an idea which is completely opposite to the idea of obtaining high toughness value in the present invention.  
10 Therefore, it is noted that this reference does not affect the patentability of the present invention.

Furthermore, the publication of JP Kokai 7-153820 discloses an aluminum nitride containing yttria and having thermal conductivity of 100 W/m · K or more, but does not describe  
15 a particle diameter of a raw material and a diameter of sintered ceramic grains and negatives the addition of impurities, and also does not refer to the annealing. Therefore, this publication does not affect the patentability of the present invention.

20 It is desirable that the ceramic substrate contains carbon in an amount of 5 to 5000 ppm in the present invention.

By incorporating carbon, the ceramic substrate can be blackened so that the radiation heat can be fully utilized when the ceramic substrate is used as a heater.

25 The carbon may be of amorphous or crystalline. In case that amorphous carbon is used, volume resistivity can be prevented from dropping at high temperature. In case that the crystalline carbon is used, thermal conductivity can be prevented from dropping at high temperature. Accordingly, both  
30 crystalline carbon and amorphous carbon may be used together depending on the purpose. The content of carbon is preferably in a range of 50 to 2000 ppm.

In case that the ceramic substrate of the first aspect of the present invention contains carbon therein, it is  
35 preferable that carbon is added so that the brightness of the

aluminum nitride sintered body is N4 or less when evaluated as the value according to the definition of JIS Z 8721. The aluminum nitride sintered body having such brightness exhibits excellent heat radiation and excellently conceals the conductors and the like embedded therein.

Herein, the brightness N is defined as follows: the brightness of ideal black is made to 0; that of ideal white is made to 10; respective colors are divided into 10 parts in the manner that the brightness of the respective colors is recognized stepwise between the brightness of black and that of white at equal intensity intervals; and the resultant parts are indicated by symbols N0 to N10, respectively.

Actual brightness is measured by comparison with color chips corresponding to N0 to N10. One place of decimals in this case is made to 0 or 5.

The present invention is the ceramic substrate for a semiconductor producing/examining device, and specific examples of the devices include an electrostatic chuck, a hot plate (a ceramic heater) and a wafer prober and the like.

20           In case that a conductor formed in the ceramic substrate  
is a resistance heating element, it can be used as a ceramic  
heater (a hot plate).

Fig. 1 is a plain view schematically showing one example of the ceramic heater as one embodiment of the ceramic substrate according to the ceramic substrate for a semiconductor producing/examining device of the present invention. Fig. 2 is a partially enlarged sectional view showing a part of the ceramic heater shown in Fig. 1.

A ceramic substrate 11 is formed into a disc shape, and  
30 a resistance heating element 12 as a temperature control means  
is formed into a concentric circles-like pattern inside the  
ceramic substrate 11. Moreover, the resistance heating element  
12 is constituted so that, each of a pair of two adjacent concentric  
circles are connected, as a set of circuit, to form one line;  
35 and an external terminal 13 as the input/output terminal is

connected to each end portion of the circuit through a conductor filled through hole 19.

In addition, as shown in Fig. 2, a through hole 15 is provided on the ceramic substrate 11, and a supporting pin 26 is inserted through the through hole 15 so as to support a silicon wafer 9. When the supporting pins 26 are moved in vertical direction, the silicon wafer 9 can be received from a carrier, the silicon wafer 9 can be put on a wafer treating face 11a of the ceramic substrate 11 so as to be heated, the silicon wafer 9 can be supported in a state that it is distanced from the wafer treating face 11a with an interval of about 50 to 2000  $\mu\text{m}$  so as to be heated.

In addition, a bottomed hole 14 for inserting a temperature measuring element such as thermocouples is provided on a bottom face 11b of the ceramic substrate 11. When the resistance heating element 12 is energized, the ceramic substrate 11 is heated, and as a result, an object to be heated such as a silicon wafer and the like can be heated.

As for the ceramic substrate 11 constituting the ceramic heater 10, since a fractured section shows a state of intergranular fracture and has a high fracture toughness value, its thermal shock resistance is excellent. Moreover, in the ceramic substrate 11 which has gone through the annealing treatment and the like, impurities are segregated in the grain boundaries and, thus on the contrary, a purity of grain crystal becomes high. For this reason, the thermal conductivity thereof becomes 100 W/m $\cdot$ K or more, namely it is excellent.

In case that resistance heating element is provided inside the ceramic substrate, an opening for blowing a coolant such as air and the like as a cooling means may be provided in a supporting case into which the ceramic substrate is fitted. In case that the resistance heating element is provided inside the ceramic substrate, plural layers of them may be provided.

In this case, it is preferable that the patterns at respective layers are formed so that the patterns complement





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electrical conductivity, and includes resin, solvent, thickener and the like.

Examples of materials of the metal particles and the conductive ceramic particles are mentioned above. It is preferable that a particle diameter of the metal particle or the conductive ceramic particles is 0.1 to 100  $\mu\text{m}$ . When the particle diameter is less than 0.1  $\mu\text{m}$ , namely, too fine, the particles are easily oxidized. Meanwhile, when the particle diameter exceeds 100  $\mu\text{m}$ , the particles are less likely to be sintered, and the resistance value becomes large.

Shape of the metal particles may be of spherical or scaly. In case that these metal particles are used, mixture of the spherical and scaly particles may be used.

In case that the metal particles are the scaly particles or the mixture of the spherical and scaly particles, metal oxide between the metal particles can be easily retained, and the close contact between the resistance heating element and the ceramic substrate is ensured, and the resistance value can be large. For these reasons, they are advantageous.

As the resin to be used in the conductor containing paste, an acrylic resin, an epoxy resin, a phenol resin and the like is used. Moreover, as the solvent, isopropyl alcohol and the like is used. As the thickener, cellulose and the like is used.

When the conductor containing paste for the resistance heating element is formed on the surface of the ceramic substrate, it is preferable that metal oxide as well as the abovementioned metal particles are added into the conductor containing paste, and the metal particles and the metal oxide are sintered. By thus sintering the metal oxide together with the metal particles, the ceramic substrate and the metal particles can be adhered more closely.

The reason for the improvement in the adhesion with the ceramic substrate due to the mixing of the metal oxide is not clear. However, it is considered that the surfaces of the metal particles and the surface of the ceramic substrate composed of

When the area resistivity exceeds  $45 \text{ m}\Omega/\square$ , a calorific value becomes so large with respect to an applied voltage amount that the calorific value is hard to be controlled in the ceramic

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In this electrostatic chuck 101, an electrostatic

electrode layer, which is composed of a chuck positive electrostatic layer 2 and a chuck negative electrostatic layer 3, is embedded inside the disc-shaped ceramic substrate 1. A thin ceramic layer 4 (hereinafter, referred to as a ceramic dielectric film) is formed on the electrostatic electrode layer. Moreover, the silicon wafer 9 is put on the electrostatic chuck 101 and grounded.

As shown in Fig. 4, the chuck positive electrostatic layer 2 is composed of a semicircular arc part 2a and a comb teeth-shaped part 2b, and the chuck negative electrostatic layer 3 is also composed of a semicircular arc part 3a and a comb teeth-shaped part 3b. The chuck positive electrostatic layer 2 and the chuck negative electrostatic layer 3 are arranged so as to face each other in a state that the comb teeth-shaped sections 2b and 3b cross each other. The chuck positive electrostatic layer 2 and the chuck negative electrostatic layer 3 are connected to a + side and a - side of DC power source respectively so that a DC voltage  $V_2$  is applied thereto.

In addition, in order to control the temperature of the silicon wafer 9, the resistance heating element 5 having a concentric circles-like pattern as viewed from the above, as shown in Fig. 1 is provided inside the ceramic substrate 1. External terminals are connected and fixed to both ends of the resistance heating element 5 so that a voltage  $V_1$  is applied thereto. Also, not shown in Figs. 3 and 4, but a bottomed hole for inserting temperature measuring element therein and a through hole for inserting a supporting pin (not shown) supporting and moving the silicon wafer 9 in vertical direction therein are formed in the ceramic substrate 1 as shown in Figs. 1 and 2. Incidentally, the resistance heating element may be formed on the bottom face of the ceramic substrate.

When this electrostatic chuck 101 functions, a DC voltage  $V_2$  is applied to the chuck positive electrostatic layer 2 and the chuck negative electrostatic layer 3. As a result, the silicon wafer 9 is adsorbed and fixed to the electrodes through



the silicon/germanium-type, the bismuth/antimony-type, the lead/tellurium-type and the like.

The electrostatic chuck of the present invention has the structure shown in Figs. 3,4, for example. The material and the like of the ceramic substrate has been already described, subsequently, respective members constituting the electrostatic chuck and another embodiments of the electrostatic chuck of the present invention will be detailed below in the following description.

10           A material of the ceramic dielectric film constituting the electrostatic chuck of the present invention is not particularly limited, and an oxide ceramic, a nitride ceramic ceramic and the like can be used. Among them the nitride ceramic is preferable.

15 As the nitride ceramic, one which is the same as the ceramic  
substrate can be used, but it is desirable that the nitride ceramic  
includes oxygen. Moreover, the ceramic dielectric film is  
sintered so that intergranular fracture appears on the fractured  
section similarly to the ceramic substrate. This is because  
20 thermal shock resistance and thermal conductivity improves.

In order to incorporate oxygen into the abovementioned nitride ceramic, metal oxide is mixed with raw material powder of the nitride ceramic and then, they are fired.

Examples of the metal oxide include alumina ( $\text{Al}_2\text{O}_3$ ),  
25 silicon oxide ( $\text{SiO}_2$ ) and the like.

It is preferable that an addition amount of the metal oxide is 0.1 to 10 parts by weight with respect to 100 parts by weight of the nitride ceramic.

A thickness of the ceramic dielectric film is set to 50  
30 to 5000  $\mu\text{m}$  so that a sufficient breakdown voltage can be secured  
without lowering chuck force.

When the thickness of the ceramic dielectric film is less than  $50\text{ }\mu\text{m}$ , thus the thickness is too thin, a sufficient breakdown voltage cannot be obtained. Moreover, when the silicon wafer is put and adsorbed, insulation breakdown occasionally occurs







layer 2 and the chuck negative electrostatic layer 3 are provided between the ceramic substrate 1 and the ceramic dielectric film 4, and a metal wire 7 as the resistance heating element is embedded inside the ceramic substrate 1; as shown in Fig. 7, an electrostatic chuck 401 which is constituted such that the chuck positive electrostatic layer 2 and the chuck negative electrostatic layer 3 are provided between the ceramic substrate 1 and the ceramic dielectric film 4, and a Peltier device 8 which is composed of a thermoelectric element 81 and a ceramic plate 82 is formed on the bottom face of the ceramic substrate 1; and the like.

In the ceramic substrate constituting such electrostatic chucks, the fractured face shows a state of intergranular fracture and the fracture toughness value is large. For these reasons, the substrate has excellent thermal shock resistance.

As shown in Figs. 3 to 7, in the present embodiment, the chuck positive electrostatic layer 2 and the chuck negative electrostatic layer 3 are provided between the ceramic substrate 1 and the ceramic dielectric film 4, and the resistance heating element 5 and the metal wire 7 are formed inside the ceramic substrate 1. Thus, connecting units (conductor filled through holes) 16, 17 for connecting to external terminals are required.

The conductor filled through holes 16, 17 are formed by filling high-melting metal such as tungsten paste and molybdenum paste and the like, and conductive ceramic such as tungsten carbide and molybdenum carbide and the like.

In addition, it is preferable that a diameter of the connecting units (conductor filled through holes) 16, 17 is 0.1 to 10 mm. This is because crack and distortion can be prevented while preventing a disconnection.

The external terminals 6, 18 are connected thereto by using the conductor filled through holes as connection pads (reference to Fig. 8(d)).

The connection is carried out by using solder and blazing material. As the blazing material, silver blaze, palladium



present invention having the abovementioned structure thereinto.

The electrostatic chuck 101 is fitted into the supporting case 41 through a heat insulating material 45. Moreover, a coolant outlet 42 is formed on the supporting case 11 such that a coolant is introduced from a coolant inlet 44 and is discharged outside from an inhalation duct 43, by passing through the coolant outlet 42. By the action of the coolant, the electrostatic chuck 101 can be cooled.

Next, a method of producing an electrostatic chuck which is one example of the ceramic substrate for a semiconductor producing/examining device of the present invention will be explained below with reference to sectional views of Figs. 8(a) to (d).

(1) Firstly ceramic powder such as nitride ceramic and carbide ceramic and the like is mixed with binder and solvent so that a green sheet 50 is obtained.

As the abovementioned ceramic powder, for example, aluminum nitride powder, which is heated at 500 to 1000°C in nitrogen and hydrogen airflow so as to be subjected to a reduction process, and the like can be used. Moreover, an impurity such as boron nitride and the like can be added in a range of 0.05 to 50 ppm (in weight). It is preferable that an average particle diameter of the raw material powder is 0.1 to 1  $\mu$ m.

Here, a plurality of green sheets or one green sheet 50', which are/is laminated on the green sheet on which an electrostatic electrode layer printed body 51, mentioned later, is formed, are/is to be the ceramic dielectric film 4. For this reason, the green sheets/green sheet 50' may have a composition different from that of the ceramic substrate if necessary.

However, normally, it is desirable that the material of the ceramic dielectric film 4 is the same as the material of the ceramic substrate 1. This is because: since they are sintered together in most cases, their firing conditions are the same. However, in case that the materials are different, the method









35 Meanwhile, in order to control the temperature of the

silicon wafer, a resistance heating element 61 shown in Fig. 1 having a shape of concentric circles as viewed from the above are provided on a bottom face of the ceramic substrate 63. External terminals (not shown) are connected and fixed to both ends of the resistance heating element 61. Moreover, a guard electrode 65 and a ground electrode 66 having a lattice shape as viewed from the above (reference to Fig. 13) are provided inside the ceramic substrate 63 in order to remove stray capacitor and noise.

In the above electrostatic chuck, the resistance heating element 61 may be provided inside the ceramic substrate 63, and a material of the guard electrode 65 and the ground electrode 66 may be the same as that of the electrostatic electrode.

It is desirable that a thickness of the chuck top conductor layer 62 is 1 to 20  $\mu\text{m}$ . When the thickness is less than 1  $\mu\text{m}$ , the resistance value becomes too high, and the chuck top conductor layer 62 does not serve as an electrode. Meanwhile, when the thickness exceeds 20  $\mu\text{m}$ , the chuck top conductor layer 62 is easily exfoliated due to a stress that the conductor has.

As the chuck top conductor layer 62, at least one kind of metal selected from high-melting point metal such as copper, titanium, chromium, nickel, a noble metal (gold, silver, platinum, etc.), tungsten and molybdenum, and the like can be used.

In the wafer prober having a such a structure, after a silicon wafer on which a semiconductor circuit is formed is put, a probe card having a tester pin is pushed against the silicon wafer, and while the silicon wafer is heated and cooled, a voltage is applied thereto so that a continuity test can be conducted. Moreover, since the fractured face of the ceramic substrate shows the state of intergranular fracture, the ceramic substrate has excellent thermal shock resistance. Further, by subjecting the ceramic substrate to the annealing treatment and the like the ceramic substrate has excellent thermal conductivity.

In case that the wafer prober is produced, similarly to the electrostatic chuck for example, the ceramic substrate in



The conductor containing paste A was printed on the green sheet by screen printing so that a conductor containing paste layer was formed. A printing pattern was a concentric circle-like pattern. Moreover, a conductor containing paste layer of an electrostatic electrode pattern having a shape shown in Fig. 2 was formed on another green sheet.

Further, the conductor containing paste B was filled into the through hole for the conductor filled through hole for connecting external terminals.

34 green sheets 50' on which tungsten paste is not printed were laminated on an upper side (heating face side) of the green sheet 50 which was subjected to the above process, and 13 green sheets 50' were laminated on a lower side. The green sheet 50 on which the conductor containing paste layer having the electrostatic electrode pattern was printed was laminated thereon, and two green sheets 50' on which the tungsten paste was not printed were laminated thereon. They were pressed to be attached each other at a pressure of 80 kg/cm<sup>2</sup> at 130°C so that a lamination was formed (reference to Fig. 8(a)).

(4) Next, the obtained lamination was degreased at 600°C for 5 hours in nitrogen gas, and was hot-pressed at 1890°C for 3 hours under a pressure of 200 kg/cm<sup>2</sup> so that an aluminum nitride plate-shaped body having a thickness of 3 mm was obtained. The aluminum nitride plate-shaped body was cut out into a disc shape of 230 mm so that a plate-shaped body made of aluminum nitride, which includes the resistance heating element 5 having a thickness of 6 μm and a width of 10 mm, the chuck positive electrostatic layer 2 and the chuck negative electrostatic layer 3 having a thickness of 10 μm, was obtained (reference to Fig. 8(b)). Thereafter, the plate-shaped body was subjected to the annealing treatment at 1700°C for 3 hours.

When a fractured section of this sintered body was observed by an electron microscope (at a magnification of 2000 times), intergranular fracture was observed. Moreover, the average grain diameter was 5  $\mu\text{m}$ . Further, when the section was observed

by EPMA (made by Shimadzu Corporation: EPM-810S), Y, B and O were found in the grain boundaries.

(6) Further, the portions where the conductor filled through holes were formed were hollowed out so as to be blind holes 35 and 36 (reference to Fig. 8(c)). Next, external terminals 6,18 made of kovar were connected thereto by using the gold blazing and by conducting heating and reflowing at 700 °C (reference to Fig. 8(d)).

It is desirable that the connection of the external terminals has a structure, wherein a support of tungsten supports at three points. This is because connection reliability can be secured.

(7) Next, a plurality of thermocouples for controlling temperature were embedded in the bottomed holes thus the production of the electrostatic chuck having the resistance heating element was completed.

(Example 2) Production of an electrostatic chuck (reference to Fig. 5)

(1) Paste, which was obtained by mixing 1000 parts by weight of aluminum nitride powder (made by Tokuyama Corp., average  
25 particle diameter:  $0.6 \mu\text{m}$ ), 40 parts by weight of yttria (average  
particle diameter:  $0.4 \mu\text{m}$ ), 115 parts by weight of acrylic binder,  
0.002 parts by weight of boron nitride, 0.05 parts by weight  
of silica, 0.001 parts by weight of  $\text{Na}_2\text{O}$ , 5 parts by weight of  
dispersant and 530 parts by weight of alcohol comprising 1-butanol  
30 and ethanol, was used to be formed by the doctor blade method  
so that a green sheet having a thickness of 0.47 mm was obtained.

(2) Next, after the green sheet was dried at 80°C for 5 hours, portions which were to become through holes having diameters of 1.8 mm, 3.0 mm and 5.0 mm into which semiconductor wafer supporting pins are inserted, and portions which were to become

(3) 100 parts by weight of tungsten carbide particles having an average particle diameter of 1  $\mu$ m, 3.0 parts by weight of acrylic binder, 3.5 parts by weight of  $\alpha$ -terpineol solvent and 0.3 parts by weight of dispersant were mixed so that conductor containing paste A was prepared.

100 parts by weight of tungsten particles having average  
particlediameter of 3  $\mu$ m, 1.9 parts by weight of acrylic binder,  
10 3.7 parts by weight of  $\alpha$ -terpineol solvent and 0.2 parts by  
weight of dispersant were mixed so that a conductor containing  
paste B was prepared.

The conductor containing paste A was printed on the green sheet by screen printing so that a conductor containing paste  
15 layer composed of electrostatic electrode pattern shown in Fig.  
10 was formed.

Further, the conductor containing paste B was filled into the through holes for the conductor filled through holes for connecting external terminals.

One green sheet on which tungsten paste is not printed was laminated on an upper side (heating face side) of the green sheet which was subjected to the above process, and 48 green sheets were laminated on a lower side. They were pressed to be attached each other at a pressure of 80 kg/cm<sup>2</sup> at 130°C so that a lamination was formed.

(4) Next, the obtained lamination was degreased at 600°C for 5 hours in nitrogen gas, and was hot-pressed at 1890°C for 3 hours at a pressure of 150 kg/cm<sup>2</sup> so that an aluminum nitride plate-shaped body having a thickness of 3 mm was obtained. The aluminum nitride plate-shaped body was cut out into a disc shape of 230 mm so that a plate-shaped body made of aluminum nitride, which includes the chuck positive electrostatic layer 2 and the chuck negative electrostatic layer 3 having a thickness of 15 μm, was obtained. Thereafter, the plate-shaped body was subjected to the annealing treatment at 1700°C for 3 hours.

When a fractured section of this sintered body was observed by an electron microscope (at a magnification of 2000 times), intergranular fracture was found. Moreover, the average grain diameter was 5  $\mu\text{m}$ . Further, when the section was observed by EPMA (made by Shimadzu Corporation: EPM-810S), Y, Na, Si and O were found in the grain boundaries.

(5) A mask was placed on a bottom face of the plate-shaped body obtained in (4) and concave portions (not shown) for thermocouples were provided on the surface by a blast treatment by means of SiC and the like.

(6) Next, conductor containing paste for resistance heating element was formed on a face (bottom face) opposed to the wafer putting face. As the conductor containing paste, SOLVEST PS603D made by Tokuriki Kagaku Kenkyujo which is used for forming plated through holes of a printed circuit board was used. This conductor containing paste was silver/lead paste, and this included 7.5 parts by weight of metal oxide composed of lead oxide, zinc oxide, silica, boron oxide and alumina (their weight ratio is 5/55/10/25/5) with respect to 100 parts by weight of silver.

20 Further, the form of the silver was scaly and its average particle diameter was 4.5  $\mu$ m.

(7) The plate-shaped body on which the conductor containing paste was printed was heated and fired at 780°C so that silver and lead in the conductor containing paste are sintered and baked on the ceramic substrate 25. Further, the plate-shaped body was immersed into electroless nickel plating bath containing aqueous solution including 30g/l of nickel sulfate, 30g/l of boric acid, 30g/l of ammonium chloride and 60g/l of Rochelle salt so that a metal covering layer of nickel 25a having a thickness of 1 μm was deposited on the surface of the resistance heating element comprising the silver sintered body. Thereafter, the plate-shaped body was subjected to the annealing treatment at 120°C for 3 hours.

The resistance heating element 25 comprising silver  
35 sintered body had a thickness of 5  $\mu\text{m}$ , a width of 2.4 mm, and





hot-pressed at 1890°C for 3 hours at a pressure of 200 kg/cm<sup>2</sup> in nitrogen gas so that an aluminum nitride plate-shaped body having a thickness of 3 mm was obtained. This was cut out into a circular plate having a diameter of 230 mm so as to have a plate-shaped body. At this time, a thickness of the electrostatic electrode layer was 10 μm.

(2) This plate-shaped body is subjected to the steps (5) to (7) in the example 1 thus the electrostatic chuck 301 was obtained.

When the fractured section of this sintered body was observed by an electron microscope (at the magnification rate of 2000 times), intergranular fracture was found. Moreover, the average grain diameter was 5  $\mu\text{m}$ . Further, when the section was observed by EPMA (made by Shimadzu Corporation, EPM-810S), Y, Ca, Si and O were found in the grain boundaries.

(Example 4) Production of electrostatic chuck 401 (Fig. 7)

After the steps (1) to (5) in the example 2 were carried out, nickel was metalized on the bottom face, and a Peltier device of lead and tellurium was joined so that the electrostatic chuck 401 was obtained.

The electrostatic chuck produced in such a manner has an excellent temperature falling property, and when it was cooled by the Peltier device, the temperature drops from 450°C to 100°C in 3 minutes.

(Comparative Example 1)

(1) Paste, which was obtained by mixing 1000 parts by weight of aluminum nitride powder heated at 500°C in the air (made by Tokuyama Corp, average particle diameter: 0.6  $\mu$ m), 20 parts by weight of alumina (average particle diameter: 0.4  $\mu$ m), 115 parts by weight of acrylic binder, 5 parts by weight of polyether sulfon, 0.03 parts by weight of silica, 5 parts by weight of dispersant, and 530 parts by weight of alcohol comprising 1-butanol and ethanol, was used to be formed by the doctor blade method so that a green sheet having a thickness of 0.47 mm was obtained. Except for abovementioned part, the electrostatic chuck was obtained in the similar manner to the example 1.

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(1) Paste, which was obtained by mixing 1000 parts by weight of aluminum nitride powder (made by Tokuyama Corp, average particlediameter:  $0.6 \mu\text{m}$ ), 40 parts by weight of yttria (average particlediameter:  $0.4 \mu\text{m}$ ), 115 parts by weight of acrylic binder, 0.002 parts by weight of boron nitride, 5 parts by weight of dispersant, and 530 parts by weigh of alcohol comprising 1-butanol and ethanol, was used to be formed by the doctor blade method so that a green sheet having a thickness of 0.47 mm was obtained.

(3) 100 parts by weight of tungsten carbide particles having average particle diameter of  $1\text{ }\mu\text{m}$ , 3.0 parts by weight of acrylic binder, 3.5 parts by weight of  $\alpha$ -terpineol solvent and 0.3 parts by weight of dispersant were mixed so that conductor containing paste A was prepared.

In addition, 100 parts by weight of tungsten particles having average particle diameter of 3  $\mu$ m, 1.9 parts by weight of acrylic binder, 3.7 parts by weight of  $\alpha$ -terpineol solvent and 0.2 parts by weight of dispersant were mixed so that conductor containing paste B was prepared.

Next, a lattice-shaped guard electrode printed body and a ground electrode printed body were printed by screen printing using the conductor containing paste A.

Further, the conductor containing paste B was filled into the through holes for conductor filled through holes for connecting external terminals.

Further, 50 green sheets with and without printed bodies were laminated and then they were integrated at a pressure of 80 kg/cm<sup>2</sup> and at a temperature of 130°C so that a lamination was formed.

(4) Next, this lamination was degreased at 600°C for 5 hours in nitrogen gas, and was hot-pressed at 1890°C for 3 hours at a pressure of 200 kg/cm<sup>2</sup> so that an aluminum nitride plate-shaped body having a thickness of 3 mm was obtained. The aluminum nitride plate-shaped body was cut out into a circular shape having a diameter of 300 mm so that a plate-shaped body made of ceramic was obtained. As for the size of the conductor filled through holes 16, its diameter was 0.2 mm and its depth was 0.2 mm.

In addition, a thickness of the guard electrode 65 and the ground electrode 66 was 10 μm, and a forming position of the guard electrode 65 was 1 mm from the wafer putting face, and a forming position of the ground electrode 66 was 1.2 mm from the wafer putting face. Moreover, a size of one side of a conductor non-formed area 66a of the guard electrode 65 and the ground electrode 66 was 0.5 mm.

(5) After the plate-shaped body obtained at (4) was ground by a diamond grinder, a mask was placed thereon, and concave portions for thermocouples and grooves 76 for absorbing wafer (width: 0.5 mm, depth: 0.5 mm) were provided on the surface by the blast treatment by means of SiC and the like.

(6) Further, a layer for forming the heating element 61 was printed on a face opposed to the wafer putting face. Conductor containing paste was used for the printing. As the conductor containing paste, Solvest PS603D made by Tokuriki Kagaku Kenkyujo which is used for forming a plated through hole of a printed circuit board was used. This conductor containing paste was silver/lead paste, and this included 7.5 parts by weight of metal oxide comprising lead oxide, zinc oxide, silica, boron oxide and alumina (their weight ratio is 5/55/10/25/5) with respect to 100 parts by weight of silver.

Further, the form of the silver was scaly and its average particle diameter was 4.5 μm.

(7) The ceramic substrate on which the conductor containing paste was printed was heated and fired at 780°C so that silver and lead in the conductor containing paste are sintered and baked

on the ceramic substrate 43. Further, a heater plate was immersed into an electroless nickel plating bath comprising a solution containing 30g/l of nickel sulfate, 30g/l of boric acid, 30g/l of ammonium chloride and 60g/l of Rochelle salt, and a nickel layer (not shown), which has a thickness of 1  $\mu$ m and includes 1 weight% or less of boron, was deposited on the surfaces of the resistance heating element 61 comprising silver sintered body. Thereafter, the ceramic substrate was subjected to the annealing treatment at 120°C for 3 hours.

When the fractured section of this sintered body was observed by an electron microscope (at a magnification of 2000 times), intergranular fracture was found. Moreover, the average grain diameter was 5  $\mu\text{m}$ . Further, when the section was observed by EPMA (made by Shimadzu Corporation, EPM-810S), Y, B and O were found in the grain boundaries.

The heating element comprising silver sintered body had a thickness of 5  $\mu\text{m}$ , a width of 2.4 mm, and area resistivity of 7.7  $\text{m}\Omega/\square$ .

(8) A titanium layer, a molybdenum layer and a nickel layer were successively formed on the surface on which the grooves 67 were formed by the sputtering method. As a device for the sputtering, SV-4540 made by ULVAC Japan Ltd. was used. As for sputtering conditions, air pressure was 0.6 Pa, a temperature was 100°C, and an electric power was 200W. Sputtering time was in a range of 30 seconds to 1 minutes, and adjusted according to respective metals.

As for thickness of the films, according to an image of a fluorescence X-ray analyzer, the titanium layer was 0.3  $\mu$ m, the molybdenum layer was 2  $\mu$ m and the nickel layer was 1  $\mu$ m.

(9) The ceramic substrate obtained at (8) was immersed into electroless nickel plating bath comprising aqueous solution containing 30g/l of nickel sulfate, 30g/l of boric acid, 30g/l of ammonium chloride and 60g/l Rochelle salt. The nickel layer, which has a thickness of 7  $\mu\text{m}$  and includes 1 weight% or less

35 which has a thickness of 7  $\mu\text{m}$  and includes 1 weight% or less



particle diameter:  $0.4 \mu\text{m}$ ), 20 parts by weight of alumina, 40 parts by weight of silica, 11.5 parts by weight of acrylic binder, 0.5 parts by weight of dispersant and 53 parts by weight of alcohol comprising 1-butanol and ethanol, was used and was formed by the doctor blade method thus a green sheet having a thickness of 0.50 mm was obtained.

Thereafter, the firing temperature was set at  $1900^{\circ}\text{C}$ . Except these abovementioned parts, an electrostatic chuck was produced similarly to the example 1.

10 (Example 13)

The present example is similar to the example 1, but firing was carried out at  $1650^{\circ}\text{C}$ . When the fractured section was observed by an electron microscope (at a magnification of 2000 times), the grain diameter was  $12 \mu\text{m}$ , that is, large. It is considered that the grain diameter becomes larger as the firing temperature rises up to about  $1700^{\circ}\text{C}$ . On the contrary, it is considered that when the firing temperature exceeds  $1700^{\circ}\text{C}$ , as the temperature becomes higher, the grain diameter becomes larger.

20 In addition, even though annealing is carried out, it is not considered that impurities are discharged sufficiently, and the thermal conductivity is low.

(Example 14)

25 The present example was similar to the example 1, but green sheets which did not contain yttria were produced beforehand, and these green sheets were arranged on both sides of the lamination and the hot-pressing was carried out.

In the sintered body obtained in the present example, an impurity-existent area (reference to Fig. 17) where an impurity element (Y, O) is locally distributed in the triple points of the crystal grains and an impurity element-nonexistent area (reference to Fig. 18) where impurities do not exist in the triple points of the crystal grains coexisted. Moreover, a voltage of 5 kV was applied to the sintered body in direction of its thickness at temperatures of  $100^{\circ}\text{C}$ ,  $200^{\circ}\text{C}$ ,  $300^{\circ}\text{C}$ ,  $400^{\circ}\text{C}$  and  $500^{\circ}\text{C}$ ,

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(Example 15)

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(Example 16)

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(Example 17)

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## 5 EVALUATION METHOD

The fracture toughness value was obtained by using a Vickers hardness measuring device ("MVK-D" type manufactured by Akashi Seisakusho Co.), by pressing the indentator into the surface of the sample, measuring the length of the generated crack and performing the calculation according to the calculation formula (1) described below.

$$15 \quad = 0.026 \times E^{1/2} \times 0.5 \times P^{1/2} \times a \times C^{-3/2} \dots (1)$$

The fracture toughness values of the ceramic substrates obtained in the examples and the comparative example are listed in following tables 1 to 3.

25       The fractured sections were observed with an electron microscope at a magnification of 2000 times and whether the fractured section exhibited the state of intragranular fracture or not, was checked. Figs. 14 and 15 are scanning electron microscopic (SEM) photographs of the fractured section of  
30       fracture of the ceramic substrate obtained in the example 1 and the comparative example 1.

a. Devices used for the measurement

Thermal constant measuring device according to the Rigaku laser  
35 flush method



LF/TCM-FA8510B

b. Test conditions

Temperature: Room temperature

Atmosphere: vacuum

5 c. Measurement method

The temperature detection during the measurement of specific heat was carried out by using a thermocouple attached to the back surface of the sample with silver paste (a platinel).

10 The measurement of specific heat at the room temperature was carried out in a state in which a light-receiving plate (glassy carbon) was further attached to the upper surface of the sample through silicon grease. The specific heat ( $C_p$ ) of each sample was obtained according to the calculation formula described below.

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$$C_p = \left\{ \frac{\Delta Q}{\Delta T} - C_{p_{g.c.}} \cdot W_{g.c.} - C_{p_{s.g.}} \cdot W_{s.g.} \right\} \frac{1}{W} \quad \dots (2)$$

In the abovementioned calculation formula (2),  $\Delta Q$  represents the input energy,  $\Delta T$  represents the saturation value of the temperature rise of the sample,  $C_{p_{g.c.}}$  represents the specific heat of the glassy carbon,  $W_{g.c.}$  represents the weight of the glassy carbon,  $C_{p_{s.g.}}$  represents the specific heat of the silicon grease,  $W_{s.g.}$  represents the weight of the silicon grease,  $W$  represents the weight of the sample.

25

(4) Bending strength

The bending strength was measured by using an Instron type universal tester (4507 type, load cell: 500 kgf) in the air at 25°C, at cross head speed of 0.5 mm/min., at span distance  $L$  of 30 mm, with a thickness of test piece of 3.06 mm, with a width of the test piece of 4.03 mm. Three-point bending strength  $\sigma$  (kgf/mm<sup>2</sup>) was calculated according to the following calculating equation (3).

35

$$\sigma = \frac{3 P L}{2 w t^2} \quad \dots (3)$$



Table 2

	Firing temperature (°C)	Grain diameter of fractured section ( $\mu\text{m}$ )	Bending strength (MPa)	Fracture toughness value ( $\text{Mpa} \cdot \text{m}^{1/2}$ )	Thermal conductivity (W/mK)	Fractured section
Example 6	1710	0.5	400	3.0	170	intergranular fracture
Example 7	1750	1	450	3.0	175	intergranular fracture
Example 8	1800	3	500	3.5	185	intergranular fracture
Example 9	1890	5	500	4.0	190	intergranular fracture
Example 10	1900	10	300	2.8	185	intergranular fracture
Example 11	1950	15	280	2.5	180	intergranular fracture
Example 12	1900	8	700	7.0	40	intergranular fracture
Example 13	1650	12	285	2.6	170	intergranular fracture

Table 3

	Fracture toughness value (Mpa · m <sup>1/2</sup> )	Thermal conductivity (W/mK)	Fractured section
Example 14	4.3	200	intergranular fracture
Example 15	4.5	200	intergranular fracture
Example 16	4.4	200	intergranular fracture
Example 17	4.4	200	intergranular fracture

As is clear from the tables 1 to 3, regarding the electrostatic chucks and wafer probers with a hot plate according to the examples 1 to 17, the thermal conductivity is high, and the fractured face shows the state of intergranular fracture, thus the fracture toughness value is high. Meanwhile, in the electrostatic chuck with a hot plate according to the comparative example 1, the fracture toughness value is low and the thermal shock resistance is inferior. Also, it has low thermal conductivity.

#### Industrial Applicability

As explained above, in the ceramic substrate for a semiconductor producing/examining device of the present invention, thermal shock resistance is excellent and thermal conductivity is high since high fracture toughness value can be secured. Therefore, the ceramic substrate for a semiconductor producing/examining device which is suitable for a hot plate, an electrostatic chuck, a wafer prober and the like can be provided.